

V. "The Conditions of the Reaction between Copper and Nitric Acid." By V. H. VELEY, M.A., University Museum, Oxford. Communicated by Professor ODLING, F.R.S. Received May 13, 1889.

Introduction.

About fifty years ago De La Rive* observed that pure metallic zinc but slowly enters into reaction with dilute sulphuric acid; shortly afterwards Faraday† confirmed this observation in the case of amalgamated zinc. In the course of some investigations on the equivalent of this metal, Ramsay and Reynolds‡ failed to obtain any hydrogen from sulphuric acid and samples of zinc which they had purified by every possible precaution. Thus the evolution of hydrogen from zinc and sulphuric acid depends initially upon the presence of some third substance, be it an impurity of the acid or of the metal.

Similarly Russell§ has also observed that metallic silver is slowly attacked by nitric acid freed from any considerable quantity of nitrous acid, and that the rate with which the change proceeds depends upon the proportion of nitrous acid present.

Reactions between Copper and Nitric Acid.

The changes which take place when metallic copper is dissolved in nitric acid have attracted the attention of a number of investigators; the complexity of these changes and their almost infinite variety produced by slight variations of the conditions, are evidenced by the elaborate researches of Deville,|| Armstrong¶ with Acworth and Divers.** In the present communication I have the honour of laying before the Royal Society a short and preliminary account of some experiments on the conditions necessary for a reaction to take place between metallic copper and nitric acid.

The Methods of Experiment.

By means of a mechanical device, described fully in another paper before the Chemical Society, spheres of the purest electrotype copper procurable were placed on a small glass dish which was kept continually revolved in dilute nitric acid; a fairly uniform current of

* 'Annales de Chimie,' vol. 43, 1830, p. 425.

† 'Experimental Researches,' Series VII, p. 863.

‡ 'Chem. Soc. Journ.,' 1887 (Trans.), p. 854.

§ 'Chem. Soc. Journ.,' 1874, p. 3.

|| 'Compt. Rend.,' 70, pp. 20 and 550.

¶ 'Chem. Soc. Journ.,' 1877, p. 54.

** 'Chem. Soc. Journ.,' 1883, p. 443.

carbonic acid was also passed through the liquid to ensure its perfect agitation, and thus to remove the products of the reaction from the immediate vicinity of the metal.

The nitric acid was made up in considerable quantity at a time by diluting acid of sp. gr. 1·41 with a suitable proportion of water; the specific gravity of the diluted acid was taken by means of a very delicate pyknometer of the form devised by Sprengel, and the amount of free acid determined in the same portion by the ordinary process of acidimetry. The weight of the copper sphere, as also its diameter, was determined before and after each experiment, which lasted for one hour; from the diameters the mean area of metallic surface exposed was calculated; thus the amount dissolved off per unit area could be directly determined.

In some earlier experiments made with a view of ascertaining this amount, it was noticed that when the sphere of copper was introduced into the acid the evolution of gas did not commence at once, but if, other conditions remaining the same, the sphere was introduced into the acid containing in small quantities the products of the reaction of a former experiment, the evolution of gas commenced immediately. Further, the amount of copper dissolved per unit area was less in the first than in the succeeding experiments, after the products of the change had been allowed to accumulate in the acid. This will be rendered more evident by the figures given in the table below, the first two columns of which contain the weights of two copper spheres A and B (placed alternately in the acid) before and after each experiment, the third the differences between these two numbers, the fourth the mean area in square millimetres, and the fifth the amounts dissolved off per unit area expressed as decimilligrams per square millimetre surface, written for the sake of brevity M/A. In this and all succeeding experiments a long-range thermometer was used.

Table I.

Sp. gr. of Acid at 19° compared with Water at the same Temperature = 1·1699. Percentage of free Nitric Acid = 27·53. Temperature 25°.

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$.
4·4153 (A)	4·0768	0·3385	291·95	11·60
4·5823 (B)	4·2049	0·3774	300·05	12·38
4·0768 (A)	3·7378	0·338	275·83	12·25
4·2049 (B)	3·8465	0·3584	283·16	12·65
3·7378 (A)	3·4166	0·32125	261·23	12·37
3·8465 (B)	3·5268	0·3197	266·78	12·10
3·4166 (A)	3·1188	0·2975	246·52	12·07

It will be seen from the above table that the amount dissolved off per unit area in the first experiment is less than that in the succeeding experiments, when the products of the change were present in the acid.

In another series of experiments the nitric acid used in the first operation was rejected, and another portion of the same sample was taken for the second operation; but for those succeeding this latter was used again. It was observed that in the first two experiments the evolution of gas did not commence immediately after the introduction of the sphere into the acid, whereas in all the succeeding experiments this was the case.

Table II.

Sp. gr. of Acid at 19° = 1.1643. Percentage of Free Nitric Acid = 27.02. Temperature 20° C.

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$.
4.762	4.6519	0.1102	313.16	3.52
4.6519	4.5451	0.1068	307.29	3.48
4.5451	4.3823	0.1628	300.41	5.42
4.3823	4.2303	0.1520	293.23	5.20
4.2303	4.0838	0.1475	286.77	5.29
4.0838	3.9456	0.1383	280.15	5.05

It will be manifest from the above table that the values for the amount dissolved off per unit area on the first two experiments are concordant among themselves, as also are those of the succeeding experiments, but that those of the former are lower than those of the latter.

When copper is dissolved in nitric acid, the substance more immediately evident to the senses is cupric or cuprous nitrate or nitrite, or possibly a mixture of some of them; at first I was inclined to the belief that the copper salt was the third substance which induced the reaction between the metal and the nitric acid to start at once. Indeed, at a meeting of the Chemical Society I expressed this opinion in the course of a debate.

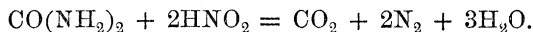
It was found subsequently that the dilute nitric acid used in the above experiments contained a small trace of nitrous acid. Accordingly a sample of nitric acid of sp. gr. 1.41 was freed from nitrous acid by passing a rapid stream of air through it at a temperature not exceeding 35° C.; during the process the acid was protected from direct sunlight. If the temperature rose to 40° C., or the acid was

not properly sheltered, nitrous acid was formed by the decomposition of the nitric acid at a rate faster than that at which it was oxidised by the air current. The acid was subsequently diluted with the required quantity of water and preserved in a dark cupboard. When 3—4 c.c. of this diluted acid were mixed with about 100 c.c. of water, no blue colour was produced on addition of starch and potassium iodide solutions, and the faintest possible orange tinge imparted to an aqueous solution of meta-phenylene diamine hydrochloride. The acid was thus free from any considerable trace of nitrous acid. Experiments similar to the above were repeated, but the current of carbonic acid omitted, in order to more precisely fix the conditions.

After introduction of a copper sphere there was no evolution of gas for three minutes, and five minutes after the reaction had set in a considerable quantity of nitrous acid was shown to be present. As regards the production of nitrous from nitric acid under these conditions, Professor Armstrong writes, in a note appended to a paper by Dr. Divers:* "With reference to the formation of N_2O_4 during the dissolution of metals, &c., I some time ago satisfied myself by experiment that it is produced . . . and there is, I believe, no doubt that, whatever the nature of the reducing agent, be it hydrogen or metal, . . . the primary product of the reduction of nitric acid is nitrous acid." This observation, made some time ago, is amply confirmed by the above and succeeding experiments. I would, therefore, merely wish to call attention to the short interval of time which elapses between the commencement of the reaction and the formation in considerable quantities of nitrous acid. Again, when the copper sphere was introduced into the acid containing the copper salt and the nitrous acid, the evolution of gas commenced at once.

In another experiment, in which the copper sphere was previously heated and then allowed to cool in a current of hydrogen to remove any superficial coating of cupric or cuprous oxide, no gas was evolved for 1' 50" after the introduction of the sphere into the acid, and 4' 30" after the reaction had set in an abundance of nitrous acid was shown to be present.

At this point, Mr. Harcourt, from a recollection of some experiments by the late Sir Benjamin Brodie, suggested to me to place into the acid a substance which should remove the nitrous acid as fast as it might be formed; urea fulfils this requirement, in that it reacts immediately with nitrous acid to form nitrogen and carbonic acid, according to the equation



Accordingly, 1 gram of urea, dissolved in 1 c.c. of water, was added to a litre of nitric acid (sp. gr. $\frac{1.9}{1.9} = 1.1662$, percentage of

* 'Chem. Soc. Journ.,' 1883 (Trans.), p. 456.

nitric acid = 27.25), into which was also placed 0.9445 gram of copper nitrate (prepared by dissolving a few of the discarded copper spheres in dilute nitric acid, evaporating the solution over the water-bath, and twice recrystallising from water). At a temperature of 25° C. no gas was evolved for 2' after insertion of the copper sphere; it was then taken out, the liquid agitated mechanically, and the sphere again introduced; no gas was evolved for 2' 50". A further quantity of 2 grams urea, dissolved in 2 c.c. water, was introduced and the experiment repeated; no gas was evolved for 7' 30". These experiments show that even in the presence of a small quantity of copper nitrate the addition of comparatively small proportions of urea will temporarily prevent the solution of the copper. It also appeared that when once the reaction had set in it could not be stopped, even though there was present in the acid more than sufficient urea to destroy the nitrous acid which might have been formed. For after agitation of the liquid the copper was again unattacked by the acid. If, then, the apparently purely local formation of nitrous acid could be prevented, it might be possible to prevent also any reaction between the copper and nitric acid from taking place.

To test this point, 1 gram of urea dissolved in 1 c.c. of water was added to a litre of nitric acid taken from the same sample as that used in the preceding experiments. The little glass dish was more quickly rotated by means of the machine, and a very rapid current of carbonic acid passed in, so that the whole liquid was kept in violent agitation. The copper sphere was introduced, the acid being heated to 25° C. During an interval of *one hour* no gas was evolved, no blue colour imparted to the acid, no alteration of the metallic surface apparent, and the loss in weight experienced was only 0.0025 gram. Whereas, if all other conditions had remained the same, except that the nitrous acid had been initially present and had been allowed to accumulate, the loss of weight from a sphere exposing a surface of 256.85 mm. would have been about 0.3 gram (calculated from the results given in Table I, the conditions of the experiments in the two cases being practically identical). This experiment might doubtless have been allowed to proceed for a longer time with the same result.

It shows, I believe, that *pure copper will not dissolve in pure dilute nitric acid*, for though the proportion of nitric acid to that of urea present was, under these conditions, 272.5:1, yet the small quantity of the latter was sufficient to completely stop the reaction. It also appears that the dissolution of copper in nitric acid is dependent solely upon the local production of nitrous acid, effected probably by local electric circuits due to traces of impurities in the copper; the proportion of nitrous acid initially produced is possibly also increased by a local rise of temperature. As regards this point Dr. Russell writes (*loc. cit.*): "The nitrous acid attacks the silver,

forming silver nitrite, nitric oxide, and water, the nitric oxide thus formed reducing hydric nitrate, and forming more nitrous acid. Thus the action gets quicker and quicker. The point still remaining to be explained is, then, how the first trace of nitrous acid is formed." My experiments, *mutatis mutandis*, are quite in accord with these observations. To test the matter further, the temperature of the same sample of acid was raised to 30° C., other experiments having shown that the amount of copper dissolved off per unit area is doubled for every 4° C. No gas was evolved for 4' after the introduction of the copper sphere, it was then taken out, and again introduced, and again no gas was evolved for 4'. The loss in weight after the 8' insertion was only 0.0025 gram, whereas it was calculated that the amount dissolved off during the interval of time, supposing the urea to have been absent, would have been 0.11 gram.

Into the same liquid a further quantity of 2 grams urea dissolved in 2 c.c. of water was added; the acid was heated to 28—28.2° C., no gas was evolved for 18'; then as the supply of carbonic acid accidentally failed, the evolution of gas from the copper started; the loss of weight observed was 0.0015 gram, a quantity which might well have been dissolved off during the interval of time which elapsed between the commencement of the reaction and the removal of the sphere from the acid. During the experiment it was interesting to observe from time to time the formation of a bubble of gas on the metallic surface, which was brushed off by the rotation of the glass dish or the stream of carbonic acid, and consequently any further reaction stopped.

As a further confirmation another sample of acid was made up, containing a slightly greater proportion of free acid, viz., 28.2 per cent., sp. gr. $\frac{1.9}{1.9} = 1.1723$; a larger sphere was taken presenting an area of 322.38 sq. mm.

The acid was heated to 27° C.; and 2 grams urea dissolved in 2 c.c. water were added. No gas was evolved for 50', and the loss of weight observed was only 0.0015 gram.

Several other similar experiments have been made with similar results, which, however, it is not considered necessary to quote.

The conclusions which I venture to think may fairly be drawn from the observations herein described are:—

(1.) The view of Professor Armstrong is corroborated that the primary product of the reduction of nitric acid by copper is nitrous acid; the latter is formed immediately after any chemical change has taken place.

(ii.) If this initial formation of nitrous acid be prevented by suitable means *copper by itself will not dissolve in dilute nitric acid by itself*.

It would follow that the production of nitric and nitrous oxides with nitrogen, in proportions varying according to the conditions, is due to subsequent changes occurring between nitrous acid and cupric or cuprous nitrate or nitrite in presence of nitric acid.

I propose to continue these researches, substituting other metals for copper, especially those which are supposed to yield primarily nitrous acid.

In conclusion, I would express my thanks to Mr. Vernon Harcourt for the suggestion which proved of so much value, and to the authorities of the University for affording me facilities for this investigation.

[*Postscript*.—Since the above was written experiments have been made in which the reaction between the copper and dilute nitric acid (sp. gr. = 1.1723), heated to 27° C., was successfully prevented for some time, even in absence of urea, by substituting a current of air for that of carbonic acid.—*May 22nd*, 1889.]

VI. "Notes on the Absorption-Spectra of Oxygen and some of its Compounds." By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received May 23, 1889.

The absorption-spectrum of oxygen has engaged attention not only on account of the important part which that element plays in the world, but because of the remarkable character of that absorption, so strongly marked, exhibiting bands of two essentially different classes, and extremely variable under varying circumstances of condensation and combination.

It may be expected that the study of it will reveal something new as to the nature of the molecular changes brought about by different circumstances, physical and chemical.

We have already published notes of some of our experiments on this subject ('Phil. Mag.,' September, 1888), and these confirm generally the observations of Egoroff, Janssen, and Olszewski.

The accompanying diagram represents the absorption of 18 metres of ordinary oxygen gas at a pressure of about 97 atmospheres, that is, of a mass of oxygen rather greater than is contained in a vertical column of equal section of the earth's atmosphere. Under the circumstances of the experiment the absorptions A and B are very black, and the lines of which they are composed appear much broader than in the ordinary solar spectrum. The other bands are all diffuse at their edges, and, so far as we have observed, unresolvable into lines. It will be noted that the complete absorption of the